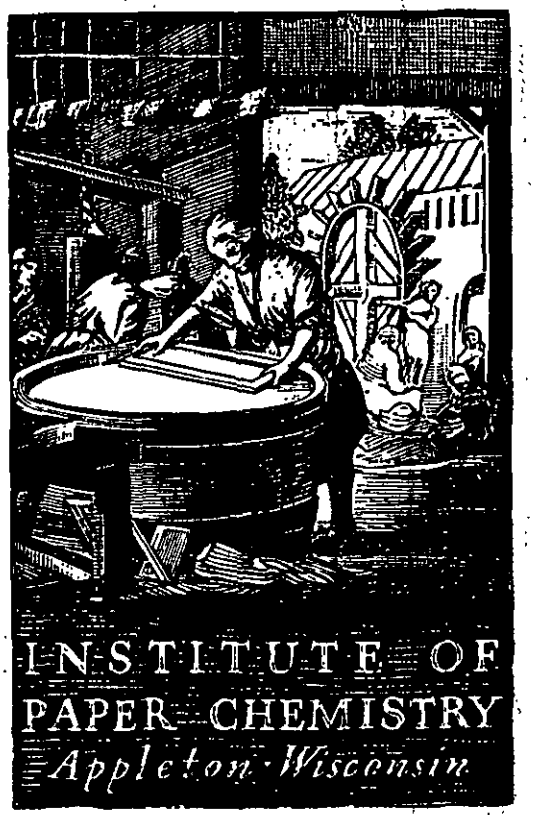




# SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

## CHEMISTRY OF HOLOLIGNIN

Research Grant

Project 2500

Report Two

A Progress Report

to

The Grantors

ALBEMARLE PAPER COMPANY
KIMBERLY-CLARK CORPORATION
SCOTT PAPER COMPANY
UNION CAMP CORPORATION
WEST VIRGINIA PULP AND PAPER COMPANY

December 1, 1966

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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## CHEMISTRY OF HOLOLIGNIN

## SUMMARY

The present study was undertaken to gain a better understanding of the changes which lignin undergoes when holopulps are prepared from aspenwood, and, hopefully, to find suitable means of estimating residual lignin in a holopulp. The results suggest that chlorine dioxide is a selective delignifying agent when high-yield pulps are prepared, but these pulps contain considerable residual lignin which is resistant to removal by further chlorine dioxide treatment Much of this residual lignin has been modified, and can be removed by sodium hydroxide extraction, although considerable carbohydrate is removed at the same time The residual lignin has been oxidized and chlorinated to some extent. It has lost some methoxyl and part of its aromatic character.

The Klason lignin determination is a poor means of estimating the lignin content of holopulps For pulps which have been extracted with sodium hydroxide after chlorine dioxide treatment, the sum of the Klason and acid-soluble lignin determinations is an approximation of the lignin content, but probably is somewhat less than the actual lignin content. Lignin removed by sodium hydroxide extraction can be estimated from the yield of acetone-soluble materials if the caustic extraction is made at room temperature. When the caustic extraction is made at 90-100°C., the acetone-solubles include materials of nonlignin origin.

## INTRODUCTION

Although a vast amount of lignin research has been carried out by many investigators in several countries, the nature of lignin as it occurs in wood is still incompletely understood. The changes which take place in the preparation of a holopulp or holocellulose are even less clear. A better understanding of these changes should be helpful in the development of a holopulping process. Estimation of the residual lignin in a pulp is often desirable, but at present reliable methods for determination of residual lignin in a holopulp are not available. The present study was undertaken in an effort to gain knowledge regarding the nature of the changes taking place in the preparation of holopulps, and hopefully to find a means of at least approximating the lignin content of a holopulp.

It is not possible to define lignin in an exact manner which is satisfactory to all workers, but, in general, the term refers to the major polymeric noncarbohydrate material in wood. It is generally considered that lignin is made up of oxygenated phenylpropane units and that it exists in wood as a cross-linked polymer, which in part is combined with carbohydrate materials. The cross-links and the lignin-carbohydrate bonds are responsible for the insolubility of the original lignin. Thus, pulping processes which depend on delignification probably require the rupture of some cross-links and some carbohydrate bonds. In addition, the introduction of solubilizing groups may be necessary, i.e., sulfonic acid groups in sulfite pulping, thio groups in kraft pulping, and new hydroxyl and carboxyl groups in oxidative pulping.

Treatment of wood with acidified chlorite, chlorine dioxide, or peracetic acid undoubtedly converts the original lignin to many different materials ranging from only slightly modified lignins to relatively simple degraded compounds

In this report the term lignin is used in a broad sense Protolignin designates the original unmodified lignin present in untreated wood Hololignin refers to the various modified and degraded materials formed from protolignin on treatment with acidified chlorite, chlorine dioxide, or peracetic acid For convenience, wood which has been treated with the various oxidizing agents is designated pulp Most of these pulps are not papermaking pulps because they cannot be defibered by simple stirring with water After a subsequent alkaline extraction, the pulps are designated residual pulp

## ISOLATION OF HOLOLIGNIN

When periodate lignin was oxidized with chlorite at pH 4, much of the undissolved product was readily soluble in 1% sodium hydroxide, and could be reprecipitated by acidification (1). Thus, it seemed likely that at least part of the lignin in holopulps could be dissolved by treating the pulp with dilute sodium hydroxide. The problem was to find suitable means of isolating the dissolved lignins. Acidification seemed necessary to liberate the free lignins from the alkaline solutions. Hydrochloric acid was selected as the acidifying agent, because sodium chloride which results from the neutralization of sodium hydroxide with hydrochloric acid is insoluble in dry acetone. Thus, it seemed that acetone might be used to separate the isolated lignins from the sodium chloride.

Several procedures were tried for the isolation of hololignin from holopulp, the goal being sharp separations with a minimum of effort. There seems to be no need to describe these in detail. Instead, the general findings are given.

Sodium hydroxide extraction at room temperature does not dissolve all of the hololignin, especially in the high-yield pulps. More lignin is dissolved when the pulp is heated with the alkali, but when this is done the final acetone-soluble lignin fraction is contaminated with materials of nonlignin origin. Evidence for this is given in the section on "Determination of Lignin in Holopulps." Unfortunately, this was not recognized until recently, and a hot extraction was used to isolate the lignins in the section on "Analytical Characterization of Hololignin."

Acidification of the alkaline extracts from the pulp precipitates some lignin along with hemicelluloses, but the precipitate is not easily separated from

the soluble materials unless considerable excess acid is used Even then it is difficult to make a clear separation of soluble and insoluble lignins Addition of acetone to the acidified extracts precipitates hemicelluloses and dissolves the lignin which has precipitated on acidification, but rather large amounts of acetone are necessary for complete precipitation of the carbohydrate fractions After precipitation of the carbohydrates, the aqueous acetone solution contains dissolved hololignins and sodium chloride. A partial separation of these can be made by dialysis after removal of the acetone, but part of the hololignin passes through the dialysis membrane along with the salt

The extracted hololignins are mostly soluble in acetone or in acetone containing small amounts of water. Consequently, the aqueous acetone solutions were evaporated to dryness under reduced pressure, and the dry residues were washed thoroughly with acetone. This generally dissolved the hololignin and left the salt as an insoluble residue.

In the first part of the study, the alkaline extracts were separated from the residual pulp, and then were acidified Acetone was added to precipitate most of the hemicelluloses In the later work, the alkaline pulp mixture was acidified directly, and acetone was added to dissolve the liberated hololignins The solution of hololignin and salt then was separated from the residual pulp and precipitated hemicelluloses. The latter procedure is preferred because the residual pulp can be washed with 90% acetone instead of water. This reduces the amount of water which has to be evaporated.

Although the isolated lignins are soluble in acetone, direct acetone extraction of the pulps removes only a small amount of the lignin An acetone extraction of Pulp-2, which is described later, gave only 0.7% extractable materials, whereas the same pulp gave an average of 14 2% acetone solubles

on extraction with sodium hydroxide at room temperature as reported later in Table IX.

The hololignins are strong acids, and it is necessary to acidify the alkaline extracts to a low pH for complete conversion of the sodium salts to the free acids. This was not recognized in the early work, and some of the fractions used for infrared and ultraviolet spectra may have consisted in part of sodium salts The sodium salts are soluble in acetone-water mixtures but not in acetone alone.

Several attempts were made to isolate hololignins from the pulping liquors, but none of the procedures used were entirely satisfactory. The liquors are believed to contain perchlorates which on concentration to dryness cause secondary reactions resulting in the evolution of considerable gas. This oxidative reaction can be prevented by treating the concentrated liquors with sulfur dioxide, but sulfuric acid is formed which darkens the products on drying. Most of the hololignin in the liquors passes through a dialysis membrane, and hence dialysis is of limited value in the isolation of lignins from the liquors.

## SPECTRAL CHARACTERIZATION OF HOLOLIGNIN

Infrared and ultraviolet absorption spectra are often used in the characterization of unknown materials. For complex materials like lignin, infrared spectra are useful for the detection of certain atomic groupings such as aliphatic and aromatic carbon-hydrogen, and carbonyl and hydroxyl groups. The ultraviolet spectra of lignin materials are more or less characteristic, but except for the indication of aromatic nature, these spectra are difficult to interpret in the case of lignin.

Substances containing phenolic hydroxyl groups show greater ultraviolet absorptivity in alkaline solutions than in neutral solution, and Goldschmid (2) suggested a method for estimating the nonconjugated phenolic hydroxyl content of lignin preparations from the increase in absorptivity at 300 nm. Both nonconjugated and conjugated phenolic hydroxyl groups show an increase in absorptivity at 250 nm. in the alkaline solutions, but a standard for the latter type was not proposed

Ultraviolet absorption is often used as a basis for quantitative analysis of soluble materials, but there are two difficulties with nonspecific materials such as lignin. establishment of a reliable standard is uncertain, and secondly contaminants which absorb at the selected wavelength are often present. Pearl and Busche (3) reviewed the estimation of acid-soluble lignin in Klason lignin filtrates from aspenwood, and suggested a standard absorptivity of 105 at 208 nm. At this wavelength interference from carbohydrate degradation products was at a minimum.

For the characterization of hololignins by means of their ultraviolet and infrared spectra, lignins were isolated from five pulps: Pulps A, B, C, D, and E. These were all prepared from aspenwood, the first three using acidified

chlorite, and the last two peracetic acid. Pulps A and B were made from alkali pretreated aspen shreds using chlorite equivalent to 67 and 12 5% chlorine dioxide, respectively, based on the wood The last three pulps were from aspenwood meal and their Klason lignin contents were 1.8, 8.5, and 0.4%, respectively

Holocelluloses were isolated from these pulps by extraction with 0 1 to 0 2N sodium hydroxide for 1 to 2 hours at room temperature. The extracts were separated from the residual pulp. After acidification, acetone was added to precipitate hemicelluloses. Two lignin fractions differing in water solubility were isolated from the aqueous acetone solutions, but the fractions designated water-soluble still contained appreciable water-insoluble material. Yields of fractions from Pulp A and Pulp C, and ultraviolet absorptivities are given in Table I. Absorptivities for a milled wood lignin (MWL) (4) are included for comparison Similar data for the lignins from the peracetic acid lignins are given in Table II. The yields for the lignins from Pulp B were 7.8% water-insoluble Lignin-5 and 1 1% water-soluble Lignin-6. The ultraviolet absorptivities for these two samples were not determined.

The data in Table I show that the absorptivities for the chlorite holocelluloses are similar to those for milled wood lignin, but generally are lower in the range from 230 to 290 nm and higher from 290 to 320 nm. There was essentially no increase in the absorptivity at 300 nm for the alkaline solutions, and thus there is no evidence for any nonconjugated phenolic hydroxyl groups. The small increase at 250 nm. may be due to a small amount of conjugated phenolic hydroxyl groups, but this is quite uncertain.

Table II indicates that the absorptivities of the peracetic acid holocelluloses are somewnat less than those of the chlorite holocelluloses This suggests

TABLE I

YIELDS AND ULTRAVIOLET ABSORPTIVITIES FOR CHLORITE HOLOLIGNINS

| | Lignin-1 | | Lignin-2 | | Lignin-3 | Lignin-4 | MWL |
|---|---|---|---|---|---|---|---|
| Isolated from pulp | A | | A | | C | C | – |
| Yield, % | 3 1 | | 1 1 | | 2 6 | 3.6 | – |
| Water solubility | Insoluble | | Soluble | | Insoluble | Soluble | – |
| Absorptivity, Wavelength, nm | Neutral Solution | Alkaline Solution | Neutral Solution | Alkaline Solution | Neutral Solution | Neutral Solution | Neutral Solution |
| 230 | 34 3 | 32 9 | 35 0 | 32 5 | 29 | 21 | 38.7 |
| 240 | 24 0 | 24.8 | 24 4 | 24.4 | 20 | 14 | 30.2 |
| 250 | 13 0 | 15.3 | 13.2 | 16.0 | 11 | 6.8 | 17 5 |
| 260 | 10.9 | 12 2 | 10 9 | 13.0 | 10 | 5 2 | 13.6 |
| 270 | 12.0 | 11.7 | 12 0 | 11.5 | 10 | 6.4 | 14 8[a] |
| 280 | 13 3 | 12 7 | 13.3 | 12.5 | 11 | 7.0 | 13 6 |
| 290 | 11.6 | 11 3 | 11.5 | 11.2 | 8 9 | 6 0 | 9.4 |
| 300 | 8.6 | 8 3 | 8 2 | 8.3 | 6.3 | 3 9 | 6 1 |
| 310 | 7.2 | 6 7 | 6.7 | 6.6 | 4 9 | 2 8 | 4 5 |
| 320 | 5.7 | 5 5 | 5 3 | 5 6 | 3.7 | 2 7 | 3 0 |

[a] Maximum 14 9 at 275 nm

TABLE II

YIELDS AND ULTRAVIOLET ABSORPTIVITIES FOR PERACETIC ACID HOLOLIGNINS

| | Lignin-P1 | Lignin-P2 | Lignin-P3 | Lignin-P4 |
|---|---|---|---|---|
| Isolated from pulp | D | D | E | E |
| Yield, % | 2.9 | 4.9 | 0.07 | 0.8 |
| Water solubility | Insoluble | Soluble | Insoluble | Soluble |
| Absorptivity· | | | | |
| Wavelength, nm. | | | | |
| 230 | 27 | 24 | 12 | 17 |
| 240 | 20 | 18 | 7.3 | 14 |
| 250 | 11 | 11 | 5.2 | 12 |
| 260 | 8.8 | 9.6 | 5.4 | 12 |
| 270 | 9.2 | 9.6 | 5.0 | 10 |
| 280 | 9.4 | 9.0 | 3.4 | 7.8 |
| 290 | 6 6 | 6.7 | 2.4 | 5 7 |
| 300 | 3 6 | 4.4 | 1.7 | 4.6 |
| 310 | 2.1 | 2.9 | 1.1 | 3.7 |
| 320 | 1.2 | 1.8 | 0.6 | 2.7 |

that peracetic acid destroys the aromatic groups in lignin to a greater extent than does chlorite.

Absorptivities in both Tables I and II were determined in aqueous ethanol solutions.

Initially, ultraviolet absorption seemed to offer promise for the estimation of chlorite nololignins, provided a suitable standard could be developed.

Subsequent results, which are reported in Table V, indicated that the absorptivities of the various hololignins are quite variable. Consequently, ultraviolet absorption seems to be of only limited value for the estimation of hololignin because of a variable absorptivity and because of a lack of a suitable standard.

Infrared spectra for some of the aqueous-acetone insoluble fractions indicated that these consisted of oxidized carbohydrate materials. The infrared spectra of Lignin-1, Lignin-2, Lignin-4, and Lignin-5 were quite similar and indicated the presence of aromatic, carbonyl, and hydroxyl groups, and aliphatic carbon-hydrogen. (The spectrum of Lignin-3 was not determined.) Lignin-6, which was mostly soluble in water, showed stronger carbonyl and hydroxyl bands, but weaker bands for aliphatic carbon-hydrogen and aromatic groups. All of the spectra were somewhat similar to the spectrum of isolated native aspen lignin, except for the stronger carbonyl band and for a shift in the aromatic bands in the regions of 6.2 to 7.2 and 8.5 to 10.0 μm. This shift is probably due to a difference in pattern of substitution of the aromatic rings.

The infrared spectra of the peracetic acid hololignins like the chlorite lignins showed bands for aromatic, carbonyl, and hydroxyl groups, but the bands for the aromatic groups were not shifted from those in the spectra of isolated native lignin.

## ANALYTICAL CHARACTERIZATION OF HOLOLIGNINS

A portion of Lignin-5 was subjected to the conditions of the Klason lignin determination. The insoluble residue, corresponding to the Klason lignin, amounted to only 36.4% The ultraviolet absorptivity of the filtrate indicated an acid-soluble lignin content of 40 to 47%. Analysis for carbohydrates indicated a total of 1.2 to 1.3%. Xylan accounted for about two thirds of the carbohydrate, arabin for one fourth, and galactan and glucan for the remainder. Roughly 20% of the sample is unaccounted for by the above values. Since this lignin was isolated by a room temperature sodium hydroxide extraction, this difference is believed to be due to the inadequacy of the ultraviolet measurements for lignin estimation.

In all of the above isolations, the lignin fractions may have been contaminated with small amounts of materials which originated in the extractives present in the original wood. For a more complete characterization, it seemed desirable to eliminate this possibility by preparing a pulp from preextracted wood.

Aspenwood shavings containing about 50% moisture were extracted directly with ethanol – benzene 1 2 in a Soxhlet extractor The extract amounted to 3.9% of the original wood (o.d basis). The extracted wood was washed once with acetone and three times with water. Some of the fines were discarded during the washing. The final material, which is referred to as extracted wood, was analyzed for Klason lignin and acid-soluble lignin

Pulp-1 was prepared by treating the extracted wood with sodium chlorite and acetic acid equivalent to 18% chlorine dioxide for 6 hours at 50°C. The final chlorite liquor had a pH of 3 6, and was treated with sulfur dioxide in an effort

to reduce any chlorate which was present. The pulp yield was 88 8% based on the unextracted wood.

PREPARATION OF LIGNIN FRACTIONS

An aliquot of the chlorite liquor from Pulp-1 was evaporated nearly to dryness, and the moist residue was extracted with acetone Evaporation of the solution gave a residue which on drying liberated large numbers of small gas bubbles and a nitric acidlike odor suggesting that additional chlorine dioxide was liberated. The dry product was extracted with acetone and a small amount of acetone-insoluble material was discarded. The final product was light in color. The formation of gas and also the analytical data suggest that this product underwent secondary reactions during its isolation. It is referred to as Lignin-7. Evidently, the sulfur dioxide treatment of the dilute liquor did not remove all of the oxidizing agents in the liquor.

In an attempt to avoid the secondary reaction, another one-fifth aliquot of the liquor was concentrated to about 100 ml and this solution was saturated with sulfur dioxide. The solution was evaporated nearly to dryness under reduced pressure, and the residue was dried in a vacuum desiccator containing potassium hydroxide. There was no evolution of gas, but there was a decided odor of hydrogen chloride, and the final product was very dark in color Thus, there may have been some decomposition due to the hydrogen chloride. This product was dissolved in acetone (10 ml per gram), and the solution was added dropwise to absolute ether with stirring (20 ml ether per ml. solution). The material which precipitated was washed three times with ether, and the final product was designated Lignin-8. The material which remained in the ether-acetone solution was designated Lignin-9 Approximately 70% of the latter fraction was

readily soluble in ether. This fraction amounted to about 6% of the pulp, but it was not obtained in a dry condition and was not characterized. The yields of the other fractions are given in Table III.

Lignin fractions were isolated from an aliquot of the pulp. In an effort to minimize alkaline oxidation, the pulp was evacuated in a desiccator, water was added, and the mixture was kept under vacuum for 0.5 hour to remove most of the air. After release of the vacuum, the surface of the mixture was swept with nitrogen until the acidification step. Sufficient 3N sodium hydroxide was added to make the mixture 0.5N with respect to alkali. After 15 minutes at room temperature, the mixture was heated in a steam cone for one hour. After cooling to room temperature, the mixture was acidified with 3N hydrochloric acid, and 2 volumes of acetone were added. The mixture was filtered, and the residual pulp, which consisted of fiber bundles, was washed with acetone – water 2 1 and finally with water. The yield of residual pulp was 63.0% based on the original unextracted wood.

The aqueous acetone solution from above was concentrated, and the resulting aqueous solution was dialyzed against distilled water for 7 days with a change of water each day. The solutions from outside of the dialysis bag were evaporated to dryness, and the residues were extracted with acetone. The acetone-extracted materials were combined to give a fraction designated Lignin-10.

The material remaining in the dialysis bag consisted of a water solution and a light brown-colored insoluble material. These were separated, and each was reduced to dryness. The residue from the water solution was not appreciably soluble in acetone, but was mostly soluble in 90% acetone. This part was designated Lignin-11.

TABLE III

YIELDS AND ANALYTICAL DATA

| | Yield[a] | Klason Lignin, % | Acid-Soluble Lignin, % | Methoxyl, % | Acid Number[b] I | II |
|---|---|---|---|---|---|---|
| Extracted wood | 96.1 | 18.0 | 3.8 | -- | -- | -- |
| Pulp-1 | 88.8 | 5.2 | 8.0 | -- | -- | -- |
| Fractions from liquor: | | | | | | |
| Lignin-7 | 10.5 | 0.0 | 21.2 | 4.9 | 78 | 258 |
| Lignin-8 | 4.6 | 19.6 | 43.2 | 10.5 | 52 | 117 |
| Fractions from pulp: | | | | | | |
| Lignin-10 | 8.3 | 11.9 | 42.3 | 9.7 | 50 | 283 |
| Lignin-11 | 1.5 | 34.9 | 33.8 | 18.5 | 20 | 114 |
| Lignin-12 | 5.7 | 57.6 | 22.4 | 18.9 | 24 | 101 |
| Residual pulp | 63.0 | 0.05 | 0.95 | -- | -- | -- |

[a]Expressed as percentage of the original unextracted wood, o.d. basis.

[b]Values under Column I correspond to the first inflection point, those under II to the total titration, expressed as milligrams of KOH per gram of sample.

The water-insoluble fraction from the dialysis bag was partly soluble in acetone, and was almost completely soluble in 95% acetone. This fraction was designated Lignin-12. Yields of the above fractions are given in Table III, and the isolation scheme is summarized in Fig. 1.

ANALYTICAL DATA

Analytical data for the wood, pulp, and various isolated fractions are given in Tables III and IV. Klason lignin, acid-soluble lignin, sugars, and methoxyl were determined by the usual Institute procedures except that for the isolated lignin fractions, 3 ml. of 72% acid was used per 50-mg. sample. For the wood and pulp, acid-soluble lignin was estimated from the maximum absorbance near 210 nm. using an absorptivity of 105 for aspen lignin at this wavelength. For the isolated lignin fractions, acid-soluble lignin was estimated from the absorbance of the Klason lignin filtrates at 280 nm using an absorptivity of 13 6 for aspen lignin.

The Klason lignin filtrates from the five isolated lignin fractions were examined for sugars by the paper chromatographic method. There was no evidence of any sugars in Lignin-7 from the liquor or in any of the three fractions isolated from the pulp . The limits of detection are about 0.2% for each sugar, and thus these fractions contain less than about 1%, if any, carbohydrate material Lignin-8 isolated from the liquor gave results indicating the presence of 0.5% glucan, 0.9% xylan, and 0.4% galactan, or 1.8% total carbohydrate There was an indication of uronic acids or other acidic material in this fraction and also in Lignin-7 and in Lignin-10 from the pulp, but not in the other two fractions from the pulp.

Approximately 50-mg. samples of the isolated lignins dissolved in 150 ml. of ethanol – water 1 1 were titrated conductometrically with 0 05N sodium hydroxide

TABLE IV

ANALYTICAL DATA

| | Carbon, % | Hydrogen, % | Oxygen, % | Chlorine | | Ash, % |
|---|---|---|---|---|---|---|
| | | | | Total, % | Water-sol., % | |
| Fraction from liquor: | | | | | | |
| Lignin-8 | 45.82 | 4.66 | 36.60 | 3.78 | 0.07 | 3.19 |
| Fractions from pulp: | | | | | | |
| Lignin-10 | 48.00 | 5.31 | 37.31 | 4.61 | -- | 0.0 |
| Lignin-12 | 53.17 | 5.64 | 30.32 | 6.75 | 0.08 | 0.21 |
| Aspen native lignin (5) | 63.2 | 5.9 | 30.9[a] | -- | -- | -- |
| Aspen milled wood lignin[b] | 61.15 | 5.87 | 32.98[a] | -- | -- | -- |

[a] By differences.
[b] From Busche's thesis (4), calculated for the lignin part of Milled Wood Lignin A.

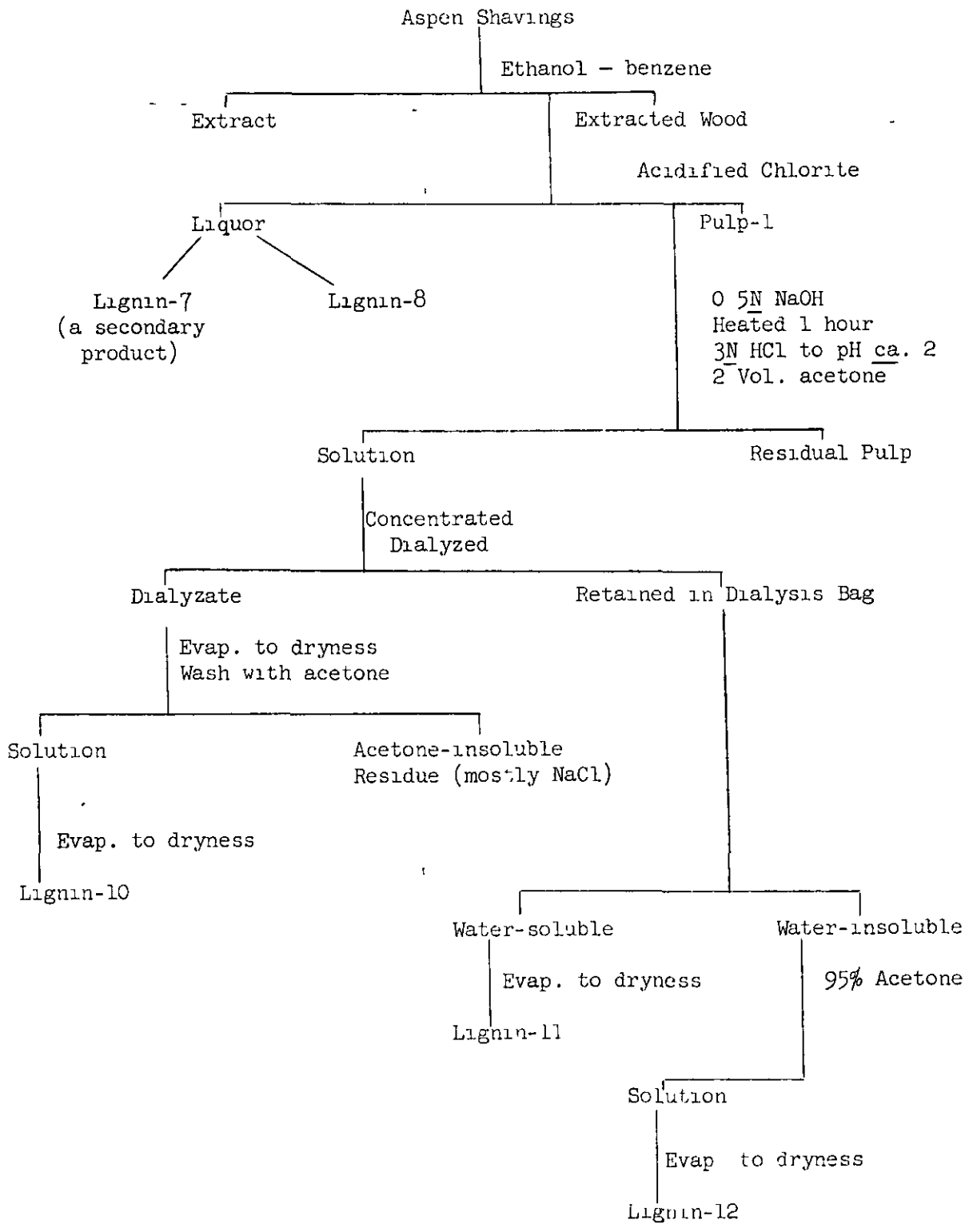


Figure 1. Isolation of Hololignins for the Characterization Study

in the same solvent. In each case, there were two inflection points in the titration curve. The results were calculated as acid numbers (milligrams of potassium hydroxide equivalent to one gram of sample).

Total chlorine was determined using the Schöniger procedure for combustion and the Volhard procedure for titration. Water-soluble chlorides were determined on two of the fractions, and are reported in Table IV These may be due to the presence of sodium chloride, although this seems unlikely in the case of Lignin-12 which was retained in the dialysis bag Water-soluble chlorides were not determined in Lignin-10 because of the absence of ash in this fraction In addition to the data in Table IV, total chlorine was determined in Lignin-7 and in Lignin-11 In these two cases, only 5-mg. samples were used, and thus the results are approximate. The results indicated 11% chlorine in Lignin-7 and 4% in Lignin-11.

The three main lignin fractions were submitted to the Geller Laboratories for determination of carbon, hydrogen, oxygen, and ash after combustion. Lignin-7 and Lignin-11 were ashed at the Institute. In order to minimize any possible loss of sodium chloride, the latter two samples were ignited first at 525°, and then were treated with sulfuric acid and reignited at 850°. Lignin-7 gave 19.4% residue at 525° and 22.1% sulfated ash, and Lignin-11 gave 3.9% ash at 525° and 5 0% sulfated ash In both cases, the residues at 525° appeared to consist largely of sodium carbonate, but the residue from Lignin-7 also seemed to contain appreciable carbonaceous material. If the sulfated values are calculated as sodium carbonate, they give 16.5% for Lignin-7 and 3.7% for Lignin-11

Ethanol – water 2 1 solutions were used for determination of the absorptivities of the isolated lignin fractions given in Table V Absorptivities

TABLE V

ABSORPTIVITY OF LIGNIN FRACTIONS

| | Absorptivity at 208 nm. | | Absorptivity at Max. | | | Absorptivity at 280 nm. | |
|---|---|---|---|---|---|---|---|
| | a | a/MeO | $\lambda_{max.}$ | a | a/MeO | a | a/MeO |
| Fractions from liquor: | | | | | | | |
| Lignin-7 | 20 | 4.1 | 211.2 | 23 | 4.7 | 1.9 | 0.39 |
| Lignin-8 | 44 | 4.2 | 210.7 | 49 | 4.7 | 8.2 | 0.78 |
| Fractions from pulp: | | | | | | | |
| Lignin-10 | 54 | 5.6 | 210.7 | 60 | 6.2 | 7.1 | 0.73 |
| Lignin-11 | 68 | 3.7 | 210.7 | 78 | 4.2 | 9.8 | 0.53 |
| Lignin-12 | 80 | 4.2 | 210.7 | 87 | 4.6 | 11.2 | 0.59 |
| Calculated from Busche's thesis | | | | | | | |
| Brauns' Native Lignin | 72[a] | 3.7[a] | 212.5 | 107 | 5.6 | 14.5 | 0.75 |
| Milled wood lignin RT | 64[a] | 3.1[a] | 212.5 | 101 | 5.0 | 13.6 | 0.67 |
| Milled wood lignin A | 60[a] | 3.1[a] | 212.5 | 98 | 5.1 | 13.3 | 0.69 |

[a]Absorptivity at 209 nm.

calculated from data in Busche's thesis (4) for other aspen lignins are included in the table. Ratios of absorptivity to methoxyl content also are given.

All samples were dried over phosphorous pentoxide in a vacuum desiccator before analysis, and except for the sugar analysis, all results are single determinations

Infrared spectra were run on the three chief lignin fractions. When compared with the spectrum of aspen native lignin, the spectrum of the water-insoluble Lignin-12 from the pulp indicated the presence of carboxyl, a greater proportion of carbonyl and hydroxyl, and less aromatic groups. The bands were not resolved as well as in the case of the native lignin. The spectra of the water-soluble Lignin-10 from the pulp and Lignin-8 from the liquor indicated still more carboxyl, carbonyl, and hydroxyl groups, and even less aromatic character.

DISCUSSION OF THE ANALYTICAL DATA

For a comparison of the different fractions with each other and with the original lignin, the ratios of the various elements to some selected reference element are useful. Carbon is the major element present and may well be taken as the reference Part of the carbon is present in methoxyl groups and some of this is lost in chlorinating Therefore, the nonmethoxyl carbon is better than the total carbon as a reference for comparison. It is believed that lignin for the most part is comprised of phenylpropane units (C-9) with more or less methoxyl attached to the phenyl groups and with variable amounts of oxygen. Calculated values based on a nonmethoxyl C-9 unit are given in Table VI. This should not imply that either the isolated lignins or the original lignin are considered homogeneous. C-9 groups as such may not be present in some of the degraded lignins, but even so the ratio of methoxyl, etc. to each 9 nonmethoxyl

TABLE VI

CALCULATED VALUES

| | Lignin-8 | Lignin-10 | Lignin-12 | Protolignin NL[a] | Protolignin MWL[b] |
|---|---|---|---|---|---|
| Carbon in lignin, g./100 g. wood | 2.6 | 4.0 | 3.0 | 13.2 | 12.8 |
| Hydrogen in lignin, g./100 g. wood | 0.21 | 0.44 | 0.32 | 1.23 | 1.23 |
| Methoxyl in lignin, g./100 g. wood | 0.48 | 0.80 | 1.08 | 4.08 | 4.44 |
| Carbon in MeO, % of sample | 4.06 | 3.76 | 7.32 | 7.55 | 8.20 |
| Non-MeO Carbon, % of sample | 41.76 | 44.24 | 45.85 | 55.65 | 52.95 |
| Hydrogen (2H) in MeO, % of sample | 0.68 | 0.62 | 1.22 | 1.26 | 1.37 |
| Non-MeO hydrogen, % of sample | 3.98 | 4.69 | 4.42 | 4.64 | 4.50 |
| Unit weight/C-9[3] | 259 | 244 | 236 | 194 | 204 |
| MeO/C-9 | 0.88 | 0.76 | 1.44 | 1.22 | 1.39 |
| Non-MeO hydrogen/C-9 | 10.3 | 11.4 | 10.4 | 9.0 | 9.2 |
| Oxygen/C-9 | 5.9 | 5.7 | 4.5 | 3.7 | 4.2 |
| Chlorine/C-9 | 0.27 | 0.32 | 0.45 | -- | -- |
| Total acid groups/C-9 | 0.54 | 1.24 | 0.42 | -- | -- |

[a]Calculated from the data for aspen native lignin.

[b]Calculated from the data for milled wood lignin.

[c]C-9 represents a phenylpropane unit with variable amounts of methoxyl.

carbons is a valid basis for comparison. Since each fraction consists of a mixture of substances, the values represent only the average composition .

The composition of the original lignin in the wood cannot be determined directly. In Table VI values for the original protolignin are based on data for an isolated native lignin (5) and for a milled wood lignin (4). The former represented only a very small part of the total lignin, and the latter had to be corrected for the presence of about 10% carbohydrate material. Thus, the data for the protolignin are open to some question. Lignin-8 was not corrected for the small amount of carbohydrate which it contained, because such a correction would not have any significant effect on the data given in Table VI

The first data in Table VI suggest that approximately 75% of the original lignin carbon and 50-60% of the original lignin methoxyl were recovered in the three lignin fractions Nearly 80% of the hydrogen seemed to be recovered, but some hydrogen was probably added during the chloriting, as a result of chain splitting. It was considered that in the loss of methoxyl the first step would be the replacement of $CH_3O$ by OH, and that the net loss is one carbon and two hydrogen atoms The nonmethoxyl hydrogen was calculated on this basis.

The calculated C-9 unit weight for the isolated lignins is appreciably higher than that for the original lignin. This is due, at least in part, to the addition of oxygen and chlorine in the chlorite treatment and represents an increase in weight of 20-30%.

For a linear high polymer comprised of phenylpropane units without double bonds, there should be essentially 10 hydrogens per C-9 unit. Cross-linking, as is believed to occur in lignin, would decrease the proportion of hydrogen, whereas chain splitting would increase the hydrogen. It is interesting

to note that the calculated value for nonmethoxyl hydrogen per C-9 is less than 10 for the original lignin and somewhat more than 10 for the degraded lignins. This is in agreement with the concept that chlorite results in breaking cross-links and in chain splitting.

All of the isolated lignins have some acidity. The degree of acidity in Lignin-8 from the liquor is open to question because of the ash in this sample. If all of the ash were sodium carbonate resulting from a sodium salt, the calculated number of acid groups per C-9 would be 0.70 instead of 0.54. Similar corrections for the other two holocellulignins considered in Table VI would have little or no effect on the reported values. Corresponding acidity values for the original lignin are not available for comparison, but protolignin usually is considered to be free of carboxyl groups and to contain somewhat less than 0.4 free hydroxyl group per C-9.

Lignin-12 appears to be the least changed of the three isolated lignins. It has taken up some hydrogen, oxygen, and chlorine, but there was no apparent loss of methoxyl and only a small loss of absorbing groups. However, it did take up the largest amount of chlorine. This suggests that chlorination may be an initial step in the chlorite reactions, or that the introduction of chlorine may make the lignin more resistant to oxidation.

The sum of carbon, hydrogen, oxygen, chlorine, and ash for the holocellulignins in Table IV ranged from 94 to 96%. This suggests that there were some inaccuracies in the data, or that some element was present which was not determined. Small amounts of nitrogen may have been present, but it seems unlikely that this could amount to 4 to 6% of the fractions. The poor summations cast some doubt on the calculated values in Table VI. If, for example, the analytical results for oxygen are low, the calculated number of oxygens per C-9 would be higher. If oxygen is calculated by difference, as is often done, the calculated number of

oxygens per C-9 is 6.9, 6.4, and 5 2 for Lignin-8, Lignin-10, and Lignin-12, respectively, rather than 5.9, 5.7, and 4.5 as reported in the table. Likewise any error in the analytical values for chlorine would affect the calculated number of chlorines per C-9 -

The hot alkaline extraction used to isolate the lignins from Pulp-1 may have resulted in contamination of Lignin-10, Lignin-11, and Lignin-12, but not Lignin-8 which was isolated from the chlorite liquor. The relative influence of this possible contamination is unknown at present. In any case the values in Tables V and VI should be considered provisional rather than final.

## *DETERMINATION OF LIGNIN IN HOLOPULPS*

In Report One, the lignin content of holopulps was estimated by the Klason method. The results given in the previous section indicate that the Klason lignin accounts for only a small part of the lignin present in chlorite holopulps Klason lignin plus acid-soluble lignin is a better measure of the lignin, but this summation still seems to give results that are too low On the basis of the results of this study, it seemed likely that lignin in the holopulps might be estimated, at least approximately, by determining the amount of acetone-soluble material that could be extracted with alkali, and adding to this the Klason and acid-soluble lignin remaining in the pulp after the alkaline extraction In order to test this possibility, three pulps were prepared.

Aspen pin chips were extracted with ethanol – benzene 1 2, and the extracted wood was heated in a steam cone with 0.1N sodium hydroxide in a nitrogen atmosphere After removal of the alkaline solution, the wood was washed thoroughly with water, 0 5% acetic acid, and finally with water again

One portion of the pretreated wood was treated with sodium chlorite equivalent to 18% chlorine dioxide and acetic acid for about 7 hours at 50°C The resulting pulp, which was designated Pulp-2, was obtained in a yield of 93 0% based on the pretreated wood Another portion of the extracted and sodium hydroxide-treated wood was treated twice in the above manner except that the amount of chlorite was doubled in each treatment, equivalent to 72% total chlorine dioxide This was designated Pulp-3 Preparation of these pulps is summarized in Fig 2

In order to prepare a pulp with a still lower lignin content, a portion of Pulp-3 was rechlorited with sodium chlorite equivalent to 36% chlorine dioxide (total 108%). The mixture was heated at 45-50°C. for 40 hours during a one-week

period and then was heated at 50-55° in the same manner during the second week At the end of this period, the mixture still gave a positive test with starch iodide paper. Finally, the mixture was heated without a cover for 16 hours at 55°. This pulp was designated Pulp-4.

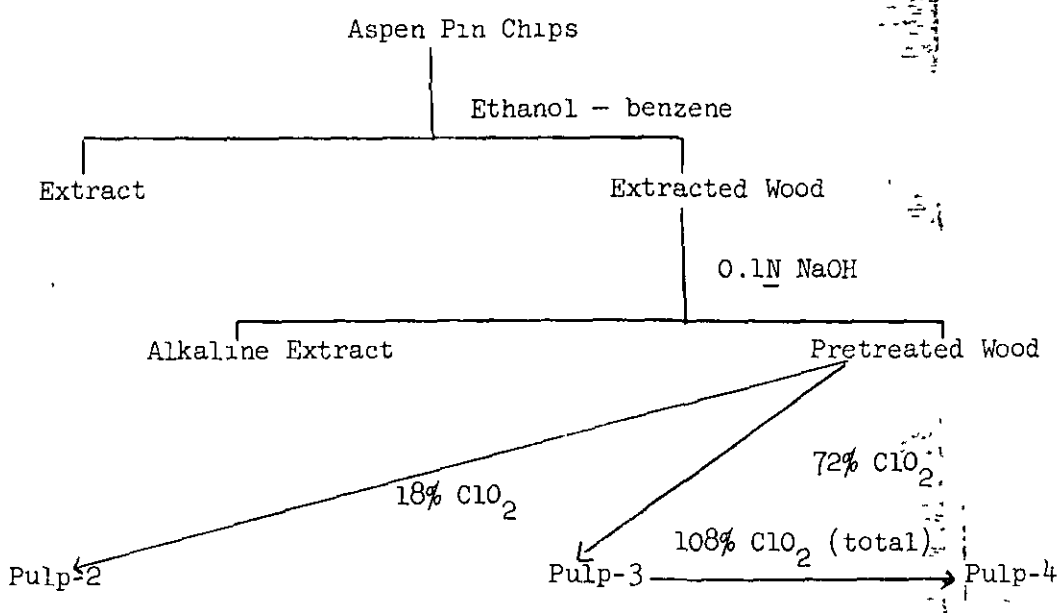


Figure 2 Preparation of Pulps for Lignin Estimation

Klason and acid-soluble lignin contents were determined for the sodium hydroxide-treated, solvent-extracted wood and for the three pulps. The results along with the pulp yields are given in Table VII The acid-soluble values were determined from the absorbance of the Klason filtrates at 208 nm. using 105 as the standard absorptivity of aspen lignin at this wavelength

TABLE VII

LIGNIN DETERMINATIONS AND YIELD

| | Pretreated Wood | Pulp-2 | Pulp-3 | Pulp-4 |
|---|---|---|---|---|
| Klason lignin, % | 18.6 | 4.8 | 0.0 | 0.0 |
| Acid-soluble lignin, % | 4.0 | 2.4 | 1.7 | 0.5 |
| Total, % | 22.6 | 7.2 | 1.7 | 0.5 |
| Pulp yield, %[a] | – | 93.0 | 72.9 | 58.2 |

[a]Percentage of the pretreated wood, o.d. basis.

The data for Pulp-2 in Table VII illustrate the unreliability of the usual lignin determination for a holopulp. Since the yield was 93%, only 7% lignin could have been removed in the pulping operation leaving 16.8% lignin in the pulp. The analytically determined value is less than half of this.

Previous results had indicated that sodium hydroxide extractions at about 100°C. removed more lignin from the holopulps than did room temperature extractions. Consequently, the first extractions were carried out at the higher temperature. The results, however, indicated that the acetone-soluble fractions from the hot extractions contained considerable material of nonlignin origin.

The hot extractions were carried out as follows: The airdry pulps were ground in a Wiley mill using a 20-mesh screen. A one-gram sample in a 25 x 200 mm. test tube was flushed with nitrogen and was kept in a nitrogen atmosphere until the acidification step. Twelve milliliters of 0.5N sodium hydroxide were added. After standing at room temperature for one hour, the mixture was heated in a steam cone for one hour. After standing at room temperature for an additional hour to cool, 2.1 ml. of 3N hydrochloric acid and 105 ml.

of acetone were added. This was sufficient acid to give a pH of about 2, and sufficient acetone to precipitate most of the hemicellulosic materials but insufficient to precipitate the sodium chloride formed on neutralization. After standing at room temperature for one hour or more to make certain that all of the acetone-soluble material had dissolved, the mixture was filtered on a tared coarse glass filter. The residual pulp containing the precipitated hemicellulose was washed with 100 ml. of 90% acetone, and finally was dried in a vacuum desiccator containing calcium chloride and concentrated sulfuric acid.

The filtrate combined with the washings was evaporated to dryness under reduced pressure. The dry residue was washed well with acetone to dissolve the acetone-soluble material, and the acetone-soluble fraction was recovered by evaporating the acetone under reduced pressure. The acetone-insoluble material was dried, weighed, and the weight corrected for the sodium chloride formed on neutralization. The remaining weight was material which had been soluble in the aqueous acetone solution but was not dissolved by acetone alone. This is designated "residue" in Tables VIII and IX.

TABLE VIII

RESULTS FOR HOT SODIUM HYDROXIDE EXTRACTIONS

| | Pulp-2 | | Pulp-3 | | Pulp-4 | |
|---|---|---|---|---|---|---|
| Residual pulp, % | 79.8 | 80.2 | 86.2 | 88.0 | 84.0 | 85.0 |
| Acetone-soluble, % | 18.8 | 18.2 | 9.9 | 8.5 | 11.6 | 10.9 |
| Residue, % | 0.6 | 0.3 | 0.5 | 0.2 | 0.0 | 0.3 |
| Summation | 99.2 | 98.7 | 96.6 | 96.7 | 95.6 | 96.2 |

TABLE IX

RESULTS FOR ROOM TEMPERATURE SODIUM HYDROXIDE EXTRACTIONS

| | Pulp-2 | | Pulp-3 | Pulp-4 |
|---|---|---|---|---|
| Residual pulp, % | 84.7 | 84.6 | 96.7 | 97.7 |
| Acetone-soluble, % | 14.1 | 14.3 | 3.4 | 1.1 |
| Klason lignin in residual pulp, %[a] | 0.9 | 0.9 | 0.0 | 0.0 |
| Acid-soluble lignin in residual pulp, %[a] | 1.8 | 1.7 | 0.4 | 0.2 |
| Total lignin, %[b] | 16.8 | 16.9 | 3.8 | 1.3 |
| Residue, % | 0.3 | 0.5 | 0.0 | 0.3 |
| Summation, %[c] | 99.1 | 99.4 | 100.1 | 99.1 |

[a]Based on the original pulp.

[b]Sum of acetone-soluble, Klason, and acid-soluble lignin in residual pulp.

[c]Sum of residual pulp, acetone-soluble, and residue.

Although the actual lignin contents of these pulps are not known it seems impossible that Pulp-4 can contain as much as 11% lignin. In addition, it seems highly unlikely that Pulp-4 contains more lignin than Pulp-3. Consequently, it was concluded that the acetone-soluble fractions of the hot sodium hydroxide extracts contain some materials of nonlignin origin, and that these fractions are not a suitable measure of the lignin content.

Room temperature sodium hydroxide extractions then were tested, and the results are given in Table IX. These extractions were made in the manner described above for the hot extractions except that the pulp was allowed to stand at room temperature for three hours with the alkali without any heating. The procedure is summarized in Fig. 3. Since the values for the acetone-soluble fractions seemed to be a more reasonable approximation of the likely lignin contents, the lignin

remaining in the residual pulps was estimated by the Klason and acid-soluble lignin procedure using a standard absorptivity of 105 at 208 nm.

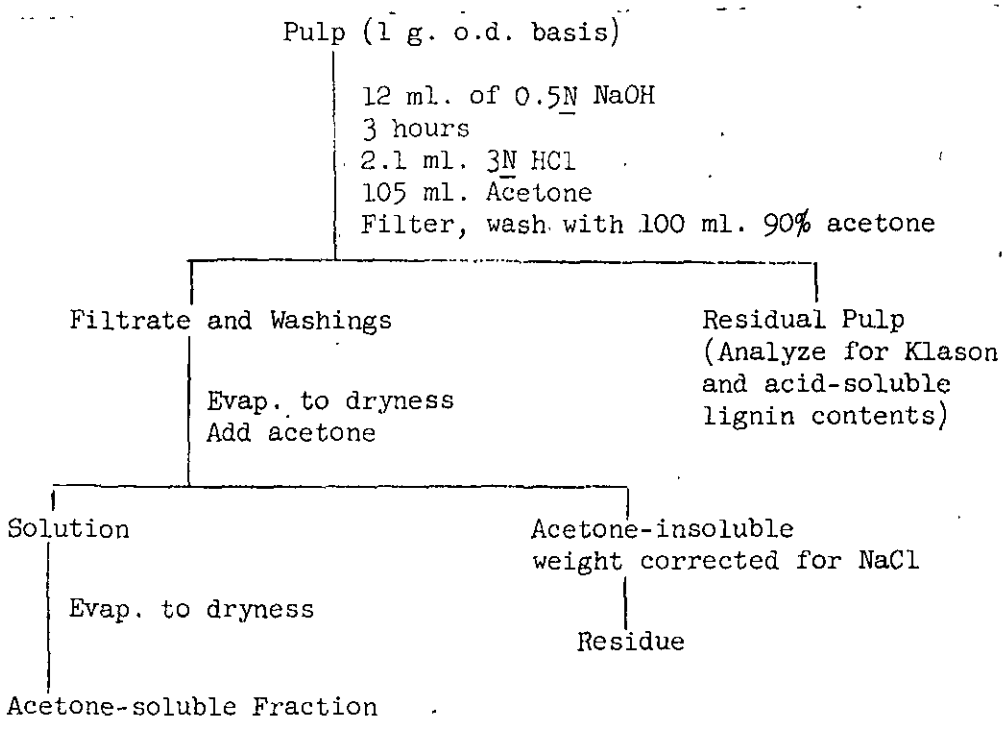


Figure 3. Estimation of Hololignin in Holopulps

The total lignin values in Table IX for Pulp-2 agree very well for the minimum lignin content estimated for this pulp, and the values for the other two pulps at least seem possible.

There are three possible sources of error in the total lignin values as determined above. Any material of nonlignin origin in the acetone-soluble fraction would give high results. Likewise, any nonlignin material which absorbed light at 208 nm. in the acid filtrate would give high results. On the other hand, the low absorptivities of the hololignins tend to make the acid-soluble lignin values low.

The above procedure was devised for "pulps" which have not been treated with alkali after the chlorite treatment. For pulps which have been defibered with alkali, the sum of Klason and acid-soluble lignin contents may be a suitable estimate of total lignin content.

## DISCUSSION AND CONCLUSIONS

The nature of the reactions taking place in the preparation of holopulps and the nature of the resulting hololignins are still quite uncertain. Consequently, some of this discussion is based on conjecture rather than on secure evidence. It seems clear, however, that the usual Klason lignin determination is a very poor estimation of total lignin in the holopulps prepared with chlorite or chlorine dioxide. Even the sum of Klason lignin plus acid-soluble lignin as determined from ultraviolet absorption is much lower than the probable lignin content. The use of ultraviolet absorbance for estimation of the hololignins is very uncertain because of variable absorptivity and because of a lack of suitable standards The results reported in Table IX for total lignin are believed to be a good approximation of the actual lignin contents, but this has not been proven.

The results suggest that lignin is selectively removed in the preparation of the high-yield pulps, but that increasing amounts of carbohydrate and decreasing amounts of lignin are removed as the pulping conditions are extended to give the lower yield pulps. The high-yield pulps are not defiberized by simple mechanical action, but require some subsequent treatment such as extraction with sodium hydroxide to convert them to a form useful for papermaking

Chlorine dioxide converts the original lignin to a series of degradation products ranging from water-soluble materials to lignin that is but little changed. Some of the residual lignin seems to be very resistant to delignification by chlorine dioxide

Chlorine dioxide causes an appreciable loss of methoxyl content This is probably not a simple demethylation, since no evidence was obtained for an increased phenolic hydroxyl content If phenolic hydroxyl groups are produced

initially, it seems likely that they subsequently undergo oxidation. The holo-lignins are strong acids and probably contain carboxyl groups. Some chlorine is introduced into the lignin. Because of the addition of oxygen and chlorine, the sum of the lignins in the chlorite liquors and in the pulp, if they could be determined accurately, should total more than the lignin in the original wood.

The loss of carbohydrates in preparation of the low-yield pulps and the nature of the nonlignin acetone-soluble materials in the hot alkali extracts both raise interesting questions. Simple delignification probably frees some carbohydrate to a soluble form, but the results suggest that some carbohydrate degradation occurs. Based on the total lignin values in Table IX, six times as much carbohydrate as lignin was removed when a portion of Pulp-3 was converted to Pulp-4. The pH of the final chlorite liquors ranged from 3.4 for Pulp-2 to 3.8 for Pulp-4, and it seems unlikely that extensive acid hydrolysis occurred. The infrared spectra for some of the hemicelluloses isolated from the holopulps indicated an oxidized condition. Thus, it seems possible that chloriting may oxidize some carbohydrate materials, and that these oxidized carbohydrates are converted in part to acetone-soluble materials on hot alkaline treatment.

ACKNOWLEDGMENTS

Pulps A, B, C, D, and E were prepared by R. B. Kesler and V Van Drunen.

Infrared and ultraviolet spectra and the various analyses were made by the following members of the Analytical Group L. G. Borchardt, Valerie Estes, Margaret Hollenback, Sue Johnson, Carl Piper, L. O. Sell, and A. Wegner. Mr. Sell interpreted the infrared spectra

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# APPENDIX

## SAMPLE DESIGNATION

In this report, designations for the isolated lignins and the pulps were not those assigned originally. To permit any possible future reference to the original work, the equivalent designations are given:

| Report Designation | Original Designation |
|---|---|
| Lignin-1 | 101B2350 |
| Lignin-2 | 102A2350 |
| Lignin-3 | 118A2350 |
| Lignin-4 | 119B2350 |
| Lignin-5 | 129D2350 |
| Lignin-6 | 129E2350 |
| Lignin-7 | 16B2475 |
| Lignin-8 | 22C2475 |
| Lignin-9 | 22D2475 |
| Lignin-10 | 18C2475 |
| Lignin-11 | 19C2475 |
| Lignin-12 | 19B2475 |
| Lignin-P1 | 124A2350 |
| Lignin-P2 | 124B2350 |
| Lignin-P3 | 119E2350 |
| Lignin-P4 | 120A2350 |
| Pulp-A | C-7 |
| Pulp-B | L |
| Pulp-C | 22 |
| Pulp-D | 20-32" |
| Pulp-E | 20-255" |
| Pulp-1 | 11B2475 |
| Pulp-2 | 74B2475 |
| Pulp-3 | 77A2475 |
| Pulp-4 | 86A2475 |